

De-sintering, A Phenomena Concurrent with Densification Within Powder Compacts: A Review

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Abstract

A morphological instability characterized by the separation of grain pairs and the disappearance of grain boundaries is a common feature in polycrystalline bodies that are constrained from shrinking during mass transport. This instability, known as de-sintering, occurs during grain coarsening as sequentially observed for thin films with columnar microstructures constrained by a substrate, fibers with a 'bamboo' microstructure constrained by a matrix, and powder matrices within composites. De-sintering is a common phenomena in partially dense, polycrystalline bodies; it occurs concurrently with densification phenomena and is emphasized in composites where the partially dense matrix is constrained from shrinking by a reinforcement network. De-sintering occurs in any lower density region where shrinkage is constrained by the average shrinkage of the body.

I. Introduction

The reader must pull out their Introduction to Ceramics (Kingery et al., 1976) and turn to pages 482 and 483 to study the consecutive micrographs, supplied by C. Greskovich and K. Lay, showing the microstructural development of alumina oxide during densification. A quick glance should tell even the casual student that grain growth can be concurrent with densification. The four micrographs on these two pages clearly show that the particle size of the initial powder compact, and the size of the grains for the partially dense compacts after heat treatments at 1700 °C for 1, 2.5 and 6 minutes. The grain size increases by about an order of magnitude between each pair of consecutive micrographs. Concurrent to this enormous amount of grain growth is a comparable growth of pores. If the large amount of grain growth does not bother the serious student, who expects to

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understand densification, the concurrent growth of the pores should trigger a lack of comprehension. That is, although the student can not read about a comprehensive link between grain growth and densification, at least the text explains grain growth in terms of either grain boundary motion or coarsening, i.e., the mass transfer between grain surfaces. On the other hand, since our Ceramic texts only show why and how pores in a powder compact can disappear during densification, it should be incomprehensible to the serious student to see them grow as clearly illustrated in the sequential micrographs supplied by Greskovich and Lay.

The objective of this review is to explain the why and how of pore growth during densification. The why and how have simple answers, but the remaining paper will detail their explanation. Why is answered by recognizing that the growth of a void can reduce the surface to volume ratio of the solid, and thus, best reduce the free energy of the system under some circumstances. How is answered by stating that just as voids can become smaller by the formation necks between touching particles, a phenomenon known as sintering, voids can also become larger (e.g., link together) when the neck and grain boundary between two grains disappear, a phenomenon described as de-sintering.

As it will be seen, the explanations to these simple answers require some constraint to shrinkage during the densification process. That is, within the body, a portion of the partially dense material needs to be partially constrained from shrinking by surrounding material. Since the voids within these regions are constrained from decreasing their free energy by shrinking, i.e., decreasing their surface to volume ratio, they, instead, decrease their free energy by coalescing to become larger. Coalescence requires grain pairs, which had previously formed necks, to de-sinter. It will also be shown that de-sintering is generally, but not exclusively, associated with grain growth. Namely, de-sintering can also occur when grain pairs are pulled apart as one region, linked to another via the grain pairs, move in opposite directions. Although the linking together of voids via de-sintering does not decrease the free energy as much as if they were to disappear, any reduction of free energy appears kinetically expedient.

The review initiates with conditions where constraint to shrinkage is more obvious, viz., where grain growth occurs in dense, polycrystalline fibers and films which are fully constrained from shrinking. It then moves to composites, where the powder matrix is either partially or fully constrained from shrinking by a reinforcement phase. The reader is then asked to return to the four micrographs

mentioned above to discover that the reason for pore growth in powder compacts is now more obvious.

2. Morphological Instability of Polycrystalline Fibers

The de-sintering phenomena associated with the instability of polycrystalline fiber is the easiest to see and explain, and has great similarity to the instability phenomena associated with grain pairs in partially dense networks. In its own right, the thermal stability of fibers is an important concern in composite materials technology. At high temperatures, the fibers can undergo grain growth. As shown elsewhere (Miller and Lange, 1989), mass transport can dramatically change the morphology of fibers, such that they become a collection of isolated grains that replaces the original fiber. This phenomenon is caused by the reduction of free energy (minimizing the interfacial energy per unit volume) that is concurrent with grain growth. Plateau (1873) was the first to show that when the length of a cylinder exceeds a critical value, its surface energy per unit volume can be decreased by breaking into spheres. Rayleigh (1945) expanded this observation into his theory of liquid jet instability to show that a cylindrical liquid jet of radius r could continuously decrease its surface energy by breaking into droplets, when subjected to symmetrical disturbances with wavelengths greater than $2\pi r$. Nichols and Mullins (1965) further extended this concept to solid rods within a solid body. These experimentally verified theories rely on the fact that large amplitude diametrical perturbations can grow by mass transport along the cylinder axis. Miller and Lange (1989) showed through theory and experiments that large amplitude perturbations in a polycrystalline cylinder, developed by grain boundary grooving, will break the fiber into individual grains provided that the mass centers of the grains are fixed, and the grain size to fiber diameter ratio exceeds a critical value.

Figure 1 illustrates a polycrystalline fiber that has undergone grain growth until the grains, assumed to be nearly identical, have equilibrium shapes, i.e., truncated spheres, shown in configuration a (assuming all interfacial energies are isotropic). For configurations a, b and c, the fiber is unconstrained and free to move. For this case, as the grain size increases, e.g., by every other grain consuming its neighbor from configuration a to b to c, the fiber will shrink to maintain a constant ratio between its surface area and its grain boundary area, which depends on the energy ratio of these two interfaces (Kellett and Lange, 1989). In this case, the grains maintain their shape as truncated spheres. It is obvious that the unconstrained fiber continuously

decreases its free energy during grain growth until it becomes a single, spherical grain.

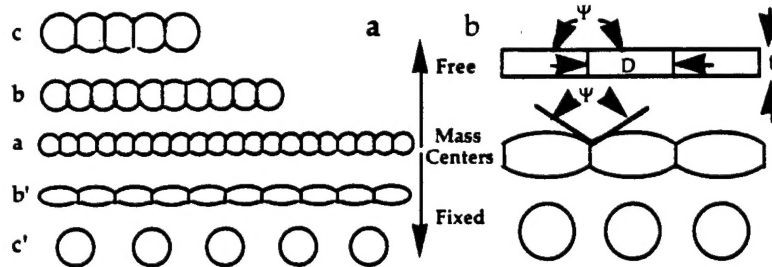


Figure 1 a) Schematic of a polycrystalline fiber that increases its grain size as its mass centers are either free to move (a, b, c) or fixed (a', b', c'). b) Configurational change as a function of the configuration angle, ψ .

For configurations a, b' and c', the fiber is constrained from shrinking, e.g., by a surrounding matrix. For this case, the ratio of the surface area to grain boundary area decreases during grain growth, the grains can not maintain their equilibrium shape as truncated spheres, and eventual, the fiber breaks into a number of isolated, spherical grains as observed in experiments (Miller and Lange, 1989).

To determine the conditions where the fiber breaks into isolated grains, Miller and Lange (1989) devised a simple model, shown in Fig. 1b, that allows the free energy change to be calculated and the determination of the equilibrium configuration of a polycrystalline fiber. The fiber is embedded within a homogeneous matrix material, which has an interfacial energy with the fiber, γ_s . The initial "bamboo" structure of the fiber is modeled by identical cylindrical grains of length D and diameter t . The aspect ratio of the grain, ' a ' = D/t , is used in subsequent calculations. The angle, ψ , defined by the surface normals at the grain boundary, is initially 180° . It was assumed that the grain centers are fixed at a distance L and that the grains develop a barrel shape during grain boundary grooving and second, each grain retains its initial mass. With these assumptions, the surface and grain boundary area of each grain can be expressed as a function of ψ , which describes the deepening of the grain boundary groove.

The total free energy of each grain is given by:

$$E = A_s \gamma_s + A_b \gamma_b \quad (1)$$

where A_s is the grain surface area, A_b is the grain boundary area, γ_s is the surface energy, and γ_b is the grain boundary energy. The surface energies are related through Young's relation:

$$\frac{\gamma_b}{\gamma_s} = 2 \cos \frac{\psi_e}{2} \quad (2)$$

where ψ_e is the equilibrium dihedral angle. The determination of A_s and A_b as a function of 'a' and ψ allows the energy of a grain, normalized by the energy of the initial, cylindrical grain to be expressed as a function of 'a' and ψ .

Figure 2a shows the normalized energy plotted as a function of the configurational angle ψ for an equilibrium dihedral angle, $\psi_e = 150^\circ$. The free energy is plotted for three grain aspect ratios; for a fixed fiber diameter, the aspect ratio will increase as the grain size increases. For each case, the free energy, E_f , is plotted as ψ decreases from 180° to the value of ψ where the grain boundary disappears. Beyond this point, the free energy is assumed to decrease continuously until it coincides with the normalized free energy of the sphere, E_s , when $\psi = 0$.

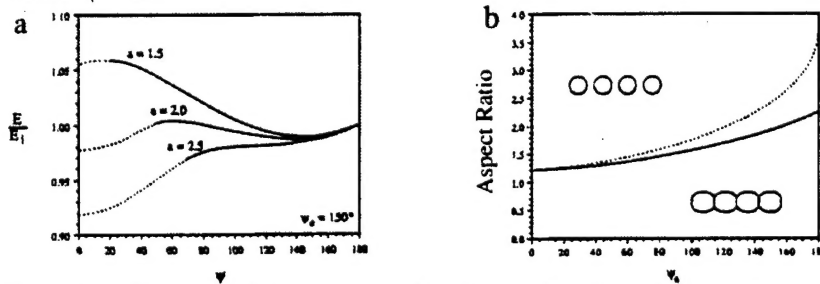


Figure 2 a) Normalized free energy of grain as a function of the configuration angle, for 3 different aspect ratios. b) Equilibrium Configurational Diagram for Fibers with different aspect ratios.

As shown in Fig. 2a, the free energy of the fiber with the smallest aspect ratio, 'a' = 1.5, decreases to a minimum while the fiber is still continuous; for this minimum ψ is near ψ_e . Since any further decrease in ψ will result in a higher free energy, the continuous fiber is the equilibrium configuration. For an increased aspect ratio of 'a' = 2, the normalized free energy again decreases to a minimum corresponding to a continuous fiber. In this case, further decreasing ψ would first increase and then decrease the free energy of the fiber, reaching another minimum for a row of spherical grains. The minimum free energy of the connected fiber is higher than that of the unconnected spheres. Thus for this case, the intact configuration is metastable; to achieve the equilibrium configuration, an energy barrier must be overcome. When the aspect ratio is further increased to 'a' = 3, the row of spherical grains again has the lowest free energy. In this case the

free energy continuously decreases with ψ . Such fibers will always break into a row of spheres, provided that mass transport can occur.

The lowest energy configuration for any given set of initial conditions can be represented with an equilibrium configuration diagram. For polycrystalline fibers, the minimum energy configuration can be displayed as regions in aspect ratio vs. equilibrium dihedral angle ('a' vs. ψ_e) space. The boundary between these regions is determined by the condition that both configurations have identical free energies as shown by the solid line in Figure 2b. Whenever the initial conditions of 'a' and ψ_e fall below this line, the lowest free energy configuration is a continuous fiber. Above this line, the lowest free energy configuration is a row of identical spheres. The region of continuous fiber metastability can also be illustrated on the equilibrium configuration diagram. In this region, which is illustrated by the middle curve 'a' = 2 in Fig. 2a, an energy barrier must be overcome. The lower bound of this region is the solid line, whereas the upper bound is the dashed line.

As shown, the instability is a natural phenomena when grain growth occurs in a polycrystalline fiber constrained from shrinking. With sufficient grain growth, the fiber will break into isolated spheres to reduce its free energy, i.e., its surface to volume ratio. If these same isolated spheres were touching one another, they would sinter together to further lower their free energy and produce one of the configurations shown in Fig. 1a for the unconstrained fiber. The ratio of free energy for the unconstrained fiber (E_u) and the constrained fiber that has broken into isolated spheres (E_c) is the energy reduction due to sintering can be expressed as [6]

$$\frac{E_u}{E_c} = \left[\frac{1}{2} \cos \frac{\psi_e}{2} \left(3 - \cos^2 \frac{\psi_e}{2} \right) \right]^{\frac{1}{3}}. \quad (3)$$

When the dihedral angle, ψ_e , is 150° , it can be seen from Fig. 2a that when grain growth occurs such that the aspect ratio 'a' becomes equal to 2.5, the constrained fiber breaks into isolated spheres to reduce its free energy by $\approx 7\%$ (free energy reduction for grain growth between 'a' = 1.5 to 2.5), whereas eq (3) shows that if the same fiber were unconstrained, it would be able to reduce its free energy by another 28%. Thus, the free energy reduction produced when the constrained fiber breaks into isolated spherical grains is significant (7%), it is only 1/5 the free energy reduction ($0.07/[0.07+0.28]$) that could have been realized if the fiber were free to shrink.

3. Morphological Instability of Polycrystalline Films

Whereas Nichols and Mullins (1965) had shown that holes would not develop in either amorphous or liquid thin films, Srolovitz and Safran (1986) were the first to show that the growth of pin holes in a polycrystalline film was possible by deepening of the groove at a three grain junction during grain growth. Miller, Lange and Marshall (1990) confirmed this idea through experiments and further developed the thermodynamics of this break-up process in the same manner described above for the polycrystalline fiber.

The break-up of a polycrystalline film into isolated grains due to grain growth is, an important problem. Generally this break-up phenomenon is unwanted, e.g., the film may be expected to either protect the underlying substrate, or carry an electric current. On the other hand, use can be made of the film after it breaks into isolated island, e.g., the isolated islands can be 'seeds' for grain growth during subsequent deposition of material (Miller and Lange, 1991).

The instability phenomena associated with polycrystalline thin films is directly analogous to that discussed above for fibers. Namely, once the grains within the film develop a columnar microstructure (each grain spans the film thickness), further grain growth will cause a free standing film to shrink. When shrinkage is constrained by the adherence to a substrate, the film will lower its free energy by eventually breaking into isolated islands. The free energy change associated with this instability can be model similar to the fiber. The initial film is assumed to be flat with a thickness t , composed of identical grains with the shape of hexagonal prisms with a center to center distance (grain size), D . The configuration angle, ψ initiates with a value of 180° and decreases during grain boundary grooving and further decreases to -180° as the isolated grain 'dewets' the substrate. (A wetting angle is defined, $\theta = (\pi - \psi)/2$, which physically explains the negative values of ψ once the grain boundaries disappear.) In the case of the polycrystalline film, the free energy per grain is given by:

$$E = A_s \gamma_s + A_b \gamma_b + A_i \gamma_i + A_{sub} \gamma_{sub}, \quad (4)$$

where subscripts s , b , i , and sub stand for surface, grain boundary, interface and substrate, respectively. Analogous to the fiber case, the different interfacial areas can be expressed in terms of the aspect ratio of the grain, (L/t) and the configuration angle, ψ . The only difference between the free energy functions for the fiber and film is the larger number variables. Similar to the fiber case the free energy (eq 4) can be expressed as a function of the configuration angle, for a specific set of

interfacial energies, expressed by ratios, and thus, by angles (analogous to the dihedral angle). Like-wise, similar to the fiber story, all information can be summarized with multi-variable, equilibrium configuration diagram where the boundaries in this diagram are conditions where two configurations (e.g., the covered and 'island' configuration) have the same free energy.

4. Constrained Densification of Powders

The densification of powder compacts containing reinforcements for ceramic matrix composites introduced the subject of constrained densification to the powder densification community. As detailed elsewhere (Lam and Lange, 1994) different models were put forth to explain the incomplete (or absence) of composite shrinkage. Figure 3a, which shows a periodic distribution of spherical, dense inclusions distributed within a powder compact can be used to explain why the reinforcements prevent the composite from achieving full density.

Consider two slices removed from the composite shown in Fig. 3a, one containing the inclusions, and one taken from between the inclusions, that only contains the powder matrix. Fig. 3b shows that if each slice were heated to allow the powder to densify, the slice containing the inclusions would shrink less because it contains a smaller fraction of the powder, which is the only phase that shrinks. In the composite, this differential shrinkage can not be tolerated unless the slices containing the inclusions were subjected to a sufficient compressive stress to cause the densifying matrix to deform into the regions where shrinkage is constrained. When the powder matrix is a crystalline material that undergoes growth as it densifies, and thus becomes very resistant to deformation by the small 'sintering stresses', high density and low density regions develop within the matrix phase during its 'densification' (Sudre and Lange, 1992).

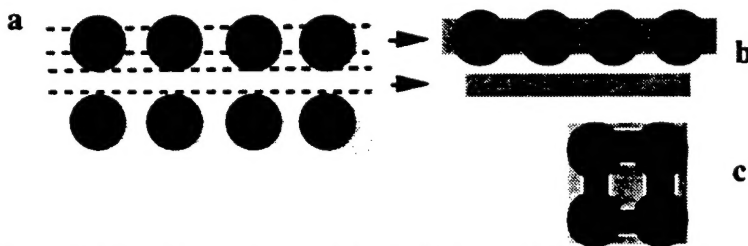


Figure 3 a) Powder matrix containing inclusions; b) Slices (dotted in composites) shrink after matrix densification; matrix slice shrinks more. c) Unit cell showing dense matrix between closer inclusions, and partially dense matrix within cell.

For the periodic array (Lam and Lange, 1994), the matrix between the inclusions with the smallest spacing (cell edges), becomes dense, whereas the matrix at the center of the cell is constrained from shrinking as shown in Fig. 4c. When the inclusions do not initially touch one another, then the composite shrinks until the matrix between the inclusions becomes fully dense. If the inclusions already form a touching network, then the composite does not shrink as the matrix undergoes densification by the development of large crack-like voids as discussed below.

Unlike the fibers and films that start off as dense bodies, the de-sintering phenomena within the powder matrix of the composite is concurrent with its densification. This seemingly contradictory statement occurs because powder regions within the matrix do fully densify, but voids within the matrix concurrently grow. As illustrated in Fig. 3c, shrinkage within the powder matrix is not uniform, i.e., dense and low density regions arise due to different constraints. In addition, cracks present in the matrix suffer large opening displacements (without growth) as opposing regions across the crack shrink in opposing directions. Observations show that two- and three-grain bridges shown in Fig. 4a,b exist between denser regions as schematically illustrated in Fig. 4c (Sudre and Lange, 1992). De-sintering is sequentially observed to occur at these bridges, causing the opposing regions to be less constrained (no longer connected to an opposing region) and allowing these regions to increase their density. When the grain bridges de-sinter, the voids appear to grow bigger. Thus, although the composite may not shrink at all, the matrix will undergo densification, where some voids within the powder matrix shrink and disappear, while others link together and grow larger.

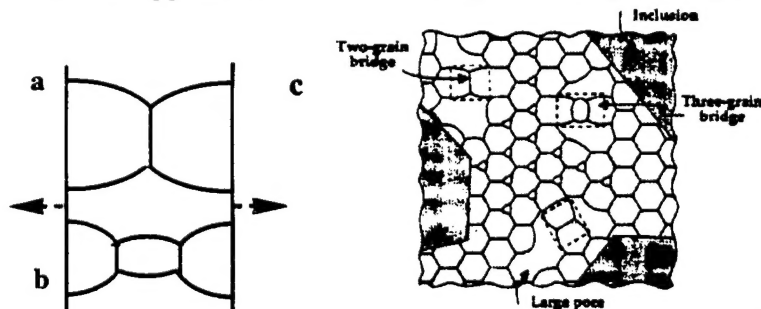


Figure 4 a) Two grain bridge and b) three grain bridge between denser regions in powder matrix phase. c) Schematic of void distribution within matrix phase, where regions are linked by two- and three-grain bridges (Sudre and Lange, 1992)

De-sintering can occur in an identical manner as illustrated above for the fiber, viz., by grain coarsening, which would be best illustrated by Fig. 4b, i.e., the disappearance of the smaller, central grain. Concurrent with grain coarsening, opposing regions will exert a tensile stress on the connecting grain pairs (arrows in Fig. 4), which, in effect, also increases their aspect ratio. Calculations that involve either coarsening, or tensile extension or both, lead to similar free energy functions as discussed above for the grain pairs in the fiber analysis, and similar configurational equilibrium diagrams. As grain become larger, new grain pairs now link other regions, and these grain pairs undergo de-sinter, to further unconstrained the densifying regions. These events are certainly not isolated, but occurs simultaneously throughout the matrix, and continue until a dense, polycrystalline matrix is formed that contain reinforcements and voids. Since the constrain to shrinkage within one regions is directional, depending on the location of neighboring inclusions, the voids tend to develop a directional character, and appear crack-like-not a good omen for a structural ceramic.

5. Concluding Remarks

As reviewed above, the microstructural instabilities associated with grain growth in fiber and film, constrained from shrinking is caused by a phenomenon where previously formed grain pairs, de-sinter to reduce their free energy. A greater free energy reduction would have been achieved if the grain pairs remained intact and their mass centers could move together during grain growth. Similar phenomena occur within the partially dense matrix of ceramic composites. Here, either non-touching or touching reinforcement networks give rise to the constraint to shrinkage. Microstructural observations of the constrained network are very similar to the micrographs shown on pages 482 and 483 of *Introduction to Ceramics* by Kingery et al. (1976) Since these micrographs are taken for a ceramic powder that does not contain reinforcements, the question arises: What gives rise to the constrain to shrinkage within a powder compact. The answer to this must be the non-uniformity of the powder compact itself, leading to connective network that densify before others, thus constraining the shrinkage of more porous regions. These denser networks are easily observed in the micrographs on pages 482 and 483.

Before this review is closed, it should be pointed out that de-sintering also occurs in two phase systems. One type of two phase system, is where the second phase is non-connective, i.e., an inclusion phase. When the 'inclusion' phase becomes mobile, i.e., diffuses as rapidly as grain boundaries move in the major phase, it collects at 4-

grain junctions (Lange and Hirlinger, 1984). For this case, the ratio of the inclusion to grain size remains constant. Since this subject would require several more pages of this review, the reader is asked to see how this is connected to the phenomenon of de-sintering. When the volume fraction of the second phase is large enough, it becomes a connective, polycrystalline, interpenetrating phase. Growth of grains within the connective, interpenetrating phase also requires de-sintering which the reader might also ponder. In fact, the second phase might be considered a void phase that does not disappear. De-sintering also occurs in powder compacts that sinter and coarsen by evaporation-condensation; in this case the size of the void phase increases with the grain size to produce larger, self-similar microstructures. Thus, as stated above, de-sintering is a pervasive phenomena.

Acknowledgments

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